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Communication—Molten Amide-Hydroxide-Iodide Electrolyte for a Low-Temperature Sodium-Based Liquid Metal Battery

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The low cost and high abundance of sodium make it an attractive choice for the negative electrode in a liquid metal battery. However, sodium has not found use in this application owing to the high solubility of the metal in its molten halides which results in poor coulombic efficiency and an unacceptably high rate of self discharge. In this work, we investigated the electrochemical behavior of the ternary eutectic of $NaNH_2$, NaOH and NaI (m.p. 127°C) and evaluated its usefulness as an electrolyte for sodium-based liquid metal batteries. Cyclic voltammetry revealed an electrochemical window of 1.3 V at 180°C. The anodic limit is set by the oxidation of amide anions to form hydrazine gas.

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Liquid metal batteries consist of two metals of different electronegativity separated by molten salt. During discharge, the battery operates through alloying an electropositive liquid metal (e.g. Mg, Na, Li, or Ca) in an electronegative metal (e.g. Bi, Pb, Sb, or Zn). The all-liquid design allows the battery to operate at high current densities ($1\ A/cm^2$)[1] with low overvoltage due to fast mass transport in the liquid state and high ionic conductivity of molten salts. Moreover, the absence of solid electrodes endows the battery with an extended service lifetime (>10,000 cycles).[2,3]

The negative and positive electrodes are selected based on melting point and density as well as the voltage associated with alloy formation, whereas the electrolyte is chosen based on melting point, metal solubility, density, ionic conductivity, and electrochemical window.[2] Metal solubility in the electrolyte varies exponentially with operating temperature. High metal solubility in the electrolyte can influence the performance of liquid metal battery through increasing electronic conductivity, which increases the rate of self-discharge leading to lower coulombic efficiency. A low-melting electrolyte (<200°C) can substantially reduce metal solubility thereby allowing batteries to be built with low-cost negative electrodes (e.g., Na, Ca) that are otherwise inaccessible at higher temperatures (>500°C). Moreover, reducing the operating temperature below 200°C can also reduce the total battery cost through savings associated with cell container, thermal insulation, and wiring.

Early work on low-melting sodium-bearing salts focused on mixtures of NaOH, NaI, and NaBr and was driven by their utility for sodium electrowinning.[4–6] The thought was that electrolysis at a lower temperature would reduce operating costs and improve process efficiency. More recently, in connection with work on sodium-based liquid metal batteries, Spatocco et al.[7] investigated a binary eutectic of NaOH and NaI as an electrolyte operable at intermediate temperature (<280°C). An electrochemical window of 2.4 volts was measured at 250°C. In contact with liquid sodium, significantly lower values of self-discharge current were observed in this melt compared to those in early Na||Bi cells operating at much higher temperatures (necessitated by their higher-melting halide electrolytes).[8] With the intention of dropping the melting point of the electrolyte even further, i.e., below 200°C, in the present study sodium amide ($NaNH_2$) was added to the hydroxide-iodide. Heredy had reported on a mixture of 52% $NaNH_2$, 38% NaOH, and 10% NaI, which we deemed attractive for its low melting temperature (127°C) and high electrical conductivity ($3.6\ S\ cm^{-1}$).[9] Of primary concern to us was the electrochemical behavior of this ternary melt.

Experimental

$NaNH_2$ (98% purity), NaOH (99.99% purity) and NaI (99.5% purity) were purchased from Sigma-Aldrich. Salts were then separately placed in Al_2O_3 crucibles. Following the dehydration process disclosed by Yurkinskii,[10] NaOH was dried under vacuum at a temperature of 550°C for 5 hours so as to remove all moisture without undesirable conversion to Na_2O. We then crushed and ground the dried electrolyte in an argon atmosphere. NaI was dried under vacuum at 250°C for an extended period of 12 hours. Omission of this drying process can result in the reaction of residual moisture with $NaNH_2$ to form ammonia and sodium hydroxide according to the reaction

$$NaNH_2 + H_2O \rightarrow NH_3 + NaOH \qquad [1]$$

It is important to note that $NaNH_2$ can react violently with oxygen to form Na_2O according to

$$4NaNH_2 + 7O_2 \rightarrow 2Na_2O + 4NO_2 + 4H_2O \qquad [2]$$

Therefore, all dried salts were stored and tested in an argon atmosphere with O_2 levels below 1 ppm. A eutectic mixture comprising 52% $NaNH_2$, 38% NaOH and 10% NaI was prepared in an Al_2O_3 crucible. The salts were heated to 200°C to promote homogenization before the final working temperature was set at 180°C. All Al_2O_3 crucibles, tungsten, low carbon steel, and Monel-400 wires were cleaned with acetone and dried under vacuum before use.

Assembled inside an argon glove box the three-electrode setup shown in Figure 1 was used to determine the electrochemical window of the melt with an AutoLab PGSTAT 302N potentiostat/galvanostat. Working electrodes of tungsten, Monel, and low carbon steel wires ($\Phi = 1$ mm) were tested against a reference electrode consisting of liquid Na in β''-Al_2O_3 (Ionotec Ltd.) and a tungsten counter electrode.

Results and Discussion

To test the viability of this electrolyte with low-melting liquid positive electrodes such as those found in a Na||Bi-Pb or Na||Bi-Sn liquid metal battery the temperature of the experiments was set at 180°C. The electrochemical window was determined by multiple voltage sweeps at different scan rates in both the cathodic and anodic directions. Figure 2 shows cyclic voltammograms on a tungsten wire. The electrochemical window of the electrolyte is greater than 1.3 V. The reduction and oxidation peaks around 0 V vs. Na (s) are attributed to sodium deposition and stripping, respectively. Integration of the current during deposition and stripping indicates 30% loss of charge. This indicates that irreversible chemical reactions, such as formation of soluble ionic compounds (e.g., intermetallic compounds, sodium

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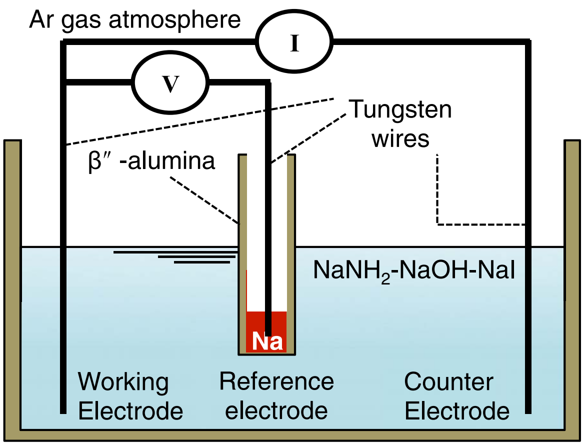

Figure 1. Three-electrode setup featuring tungsten working and counter electrodes and a reference electrode of liquid sodium in β''-Al_2O_3.

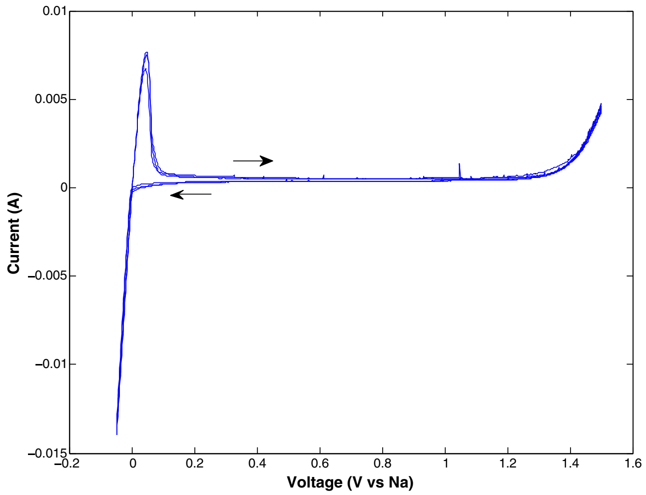

Figure 2. Cyclic voltammogram of the eutectic amide-hydroxide-iodide melt at 180°C, scan rate of 100 mV s^{-1}. Na in β''-Al_2O_3 reference electrode. Tungsten working electrode. Tungsten counter electrode.

tungsten oxides) or gas evolution (e.g., hydrogen) occur on tungsten in the negative voltage sweep.

Candidate oxidation reactions around 1.3 V are listed in Table I. The estimated voltages of reactions were calculated at 180°C using HSC (version 6). Based on the data in Table I, the limiting oxidation reaction is most likely to be the oxidation of amide ion according to Equation 3,

$$2NH_2^- = N_2H_4\,(g) + 2e^-. \qquad [3]$$

Table I. Thermodynamic calculations of candidate reactions at T = 180°C.

candidate reaction	free energy of reaction, ΔG (kJ.mol^{-1})	reaction potential, E (V) vs. Na(l)
$NaOH \Rightarrow Na + 1/2H_2O(g) + 1/4O_2(g)$	245	2.54
$NaNH_2 + NaOH \Rightarrow 2Na + NH_3(g) + 1/2O_2(g)$	388	2.01
$NaNH_2 \Rightarrow Na + 1/2N_2H_4(g)$	129	1.33

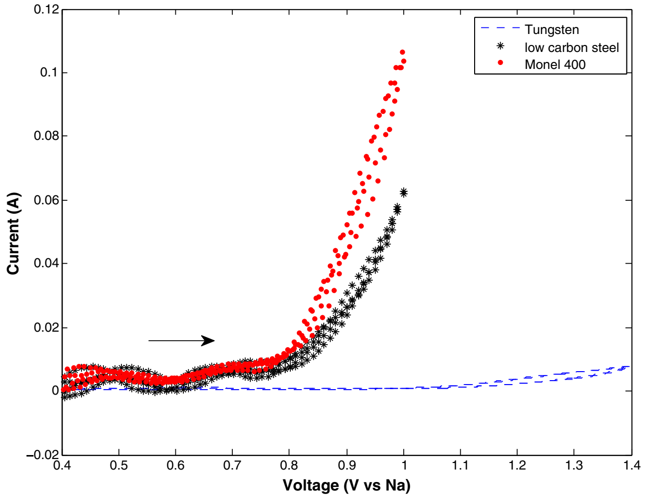

Figure 3. Anodic sweep on pure $NaNH_2$ melt at 250°C, scan rate of 100 mV s^{-1}. Na in β''-Al_2O_3 reference electrode. Three different working electrodes: tungsten (blue), low carbon steel (black) and Monel-400 (red).

To confirm that the limiting oxidation reaction is due to amide and not hydroxide, we followed the same experimental procedure while replacing the eutectic melt with pure molten $NaNH_2$. Figure 3 shows anodic sweeps performed on tungsten wire at 250°C and a scan rate of 100 mV s^{-1}. Here, the oxidation of NH_2^- follows that observed in Figure 2 with minor differences due to the effect of temperature and activity of NH_2^-. The production of hydrazine gas (N_2H_4) from the reaction poses a major safety concern. In addition to being highly toxic, hydrazine is also highly unstable and flammable. Although the measured electrochemical window of the ternary electrolyte is narrow (<1.3 V) compared to those of molten halide salts, the voltages at fully charged state of most LMBs are less than 1.25 V[2,7]; therefore, it is possible to design a cell that can safely operate without undesirable hydrazine gas evolution. Figure 3 also shows the anodic sweeps on low-carbon steel and Monel wire, which exhibit narrower electrochemical windows ~1 V which we attribute to possibly a catalytic effect on the oxidation of NH_2^-.[11] The narrow electrochemical window on the low-carbon steel was confirmed around 1 V in ternary electrolyte as expected (Figure 4). Additionally, there are clear peaks of sodium deposition and stripping around 0 V vs. Na (s). Integration of the current during deposition and stripping reveals an overall coulombic efficiency approaching 90% at a scan rate of 100 mV s^{-1}. This indicates low sodium solubility in the ternary melt and vindicates

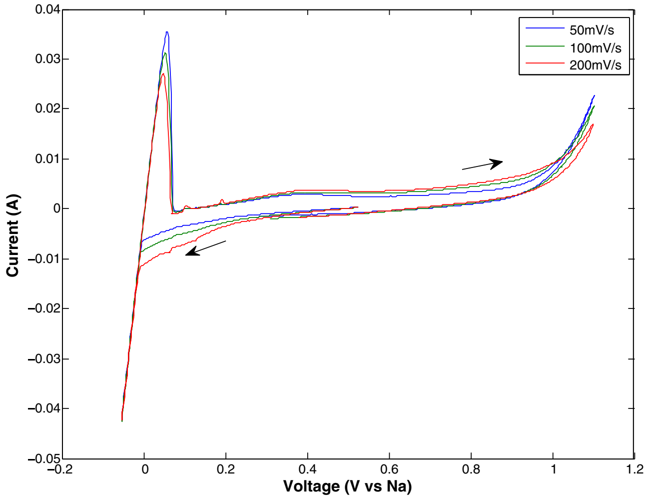

Figure 4. Cyclic voltammograms of the eutectic melt at 180°C, scan rates of 50 (blue) 100 (green) and 200 (red) mV s^{-1}. Low carbon steel working electrode measured against Na in β''-Al_2O_3 reference electrode. Current from tungsten counter electrode.

the choice of low-carbon steel as the negative current collector in liquid metal batteries. Interestingly, the overall coulombic efficiency was found to increase with decreasing scan rate. Spatocco et al. made similar observation with the binary system of NaOH and NaI.[7] These results further support Spatocco's hypothesis that deposited sodium is stabilized by a self-inhibiting reaction with NaOH making it more difficult to remove at higher scan rates.

Conclusions

The ternary mixture of 52% $NaNH_2$, 38% NaOH, and 10% NaI qualifies as a molten salt electrolyte for use in liquid metal batteries operating at temperatures below 200°C provided attention is paid to N_2H_4 mitigation (moisture level, materials of containment, and voltage limits).

Acknowledgments

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